

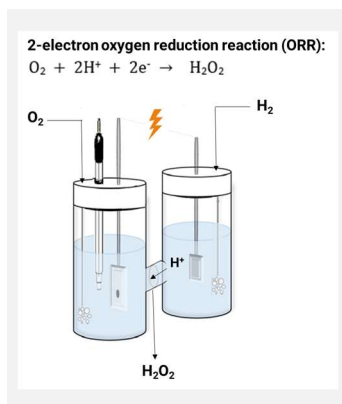
In Situ Electrochemical Generation of Hydrogen Peroxide for Water Treatment

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The electrochemical generation of hydrogen peroxide in situ eliminates the risks associated with the transport, handling, and storage of concentrated H_2O_2 solutions, enabling their safe and efficient use in the oxidation of contaminants in process streams. This study evaluated the feasibility of the in situ generation of H_2O_2 via an oxygen reduction reaction for decentralized applications in water treatment. An electrode made of carbonaceous material was used as the cathode, and its performance in generating H_2O_2 was evaluated in an H-type electrochemical cell at different current densities. The application of a current density of 20 mA/cm^2 generated H_2O_2 in concentrations of up to 350 mg/L , with 15% current efficiency and energy consumption of 171.9 kWh/kg of hydrogen produced. In general, the results demonstrated that hydrogen peroxide can be generated in situ to be integrated into advanced oxidative processes when there is a demand for H_2O_2 as a reagent.

Introduction

Hydrogen peroxide (H_2O_2) is the main reagent used in most advanced oxidation processes (AOPs) that are commonly used in water treatment, such as the Fenton (Fe^{2+}/H_2O_2), ultraviolet/ H_2O_2 (UV/ H_2O_2), and peroxone (O_3/H_2O_2) processes. Currently, more than 95% of hydrogen peroxide is produced industrially by the anthraquinone auto-oxidation process, a centralized production process that has many steps, requires complex infrastructure, generates large amounts of organic waste, and consumes significant power [1]. Furthermore, hydrogen peroxide is commercially supplied in highly concentrated solutions (35, 50, and 70 wt%), which are highly corrosive and flammable. However, for water treatment applications, the compound is used in dilute solutions (< 0.1 wt %) [2], which makes other synthesis methods preferable.

Electrosynthesis is a sustainable approach for producing in situ H_2O_2 from the 2-electron oxygen reduction reaction (ORR) in aqueous solutions, enabling the on-demand, scalable, and decentralized synthesis of H_2O_2 under mild reaction conditions (ambient temperature and pressure) without the need for any organic additives. The production of hydrogen peroxide in situ avoids the transport and storage of concentrated solutions and can considerably increase the safety and flexibility of AOPs that use H_2O_2 , enabling future applications. Another advantage of this approach is that the generation of H_2O_2 in situ occurs concomitantly with the treatment of effluents and/or oxidation of organic compounds, reducing the occurrence of secondary reactions related to the addition of high concentrations of H_2O_2 to the reaction medium and increasing efficiency of the process.

The aim of this study was to evaluate the in situ

generation of H_2O_2 by the oxygen reduction reaction for applications in water treatment. For this purpose, a cathode was prepared by functionalizing a commercial carbonaceous material to act as a gas-diffusion electrode for the electrosynthesis of H_2O_2 , and its performance was investigated in an H-type electrochemical cell at different current densities.

Material and Methods

The H_2O_2 generation experiments were conducted in a two-compartment glass reactor (H-type cell). A modified carbon GDE (oxidized Vulcan XC-72R[®]) 0.5 mg/cm^2 and Pt/C GDE 0.46 mg/cm^2 were used as the cathode and anode, respectively. The distance between the electrodes was 5.0 cm and each electrode occupied an area of 9.0 cm^2 . The two reactor compartments were separated by a proton exchange membrane (Nafion[®] NR212) with an ion exchange capacity of > 0.95 meq/g. Both compartments were filled with 100 mL of electrolyte, with 0.5 M Na_2SO_4 solution used on the cathode side and 0.1 M H_2SO_4 on the anode.

Before conducting the experiments, O_2 and H_2 were bubbled into the the cathode and anode, respectively for 20 min at a flow rate of 50 mL/min. The gas flow rate was maintained at 50 mL/min using rotameters and the pH was monitored using a multiparameter meter (Edge[®] Hanna, model HI2020-02). A Minipa[®] digital power supply (MPL-1305M) was used for all tests. Electrolysis was conducted at constant current densities (10, 20, and 30 mA/cm^2) for 120 min, and samples from the cathode compartment were collected over time to quantify the H_2O_2 formed.

The concentration of hydrogen peroxide was quantitatively analyzed using a spectrophotometric method at 446 nm [3].

Results and Discussion

The in situ hydrogen peroxide electrosynthesis experiments were carried out in constant current mode (10, 20 and 30 mA/cm²) for 120 minutes. Figure 1 shows that there was a linear increase in the concentration of hydrogen peroxide generated in the initial 20 min. Approximately 60 min after the beginning of the experiment, it was possible to notice the beginning of stabilization of the hydrogen peroxide concentration with the operating time due to the occurrence of parallel reactions, such as the self-decomposition of H₂O₂ within the solution, the reduction of H₂O₂ to H₂O at the cathode, and the H₂ evolution reaction.

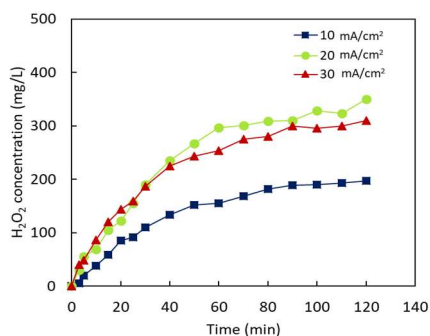


Figure 1. Electrogeneration of H₂O₂ at different current densities.

Furthermore, an increase in the current density applied during electrolysis led to an increase in H₂O₂ production. However, at a current density of 30 mA/cm², a decrease in the generation of H₂O₂ was observed, indicating that the number of electrons injected into the system may have promoted more intense competitive reactions. The application of a current density of 20 mA/cm² led to the highest concentration of hydrogen peroxide, with a maximum concentration of 350 mg/L obtained in 120 min. Another important parameter evaluated was the Faraday efficiency (FE). The FE values obtained after 120 min of the experiment at current densities of 10, 20, and 30 mA/cm² were 17, 15, and 9%, respectively (Figure 2). This result corroborates the fact that the maximum concentrations of H₂O₂ generated with current densities of 20 and 30 mA/cm² were similar, with a difference of only 11%

Conclusions

This study demonstrated the feasibility of the in situ generation of H₂O₂ via the oxygen reduction reaction for decentralized applications in water treatment. The effects of current density and power consumption were investigated. The application of a current density of 20 mA/cm² generated H₂O₂ in concentrations of up to 350 mg/L, with 15% current efficiency and energy consumption of 171.9 kWh/kg of hydrogen produced. In general, the results demonstrated that hydrogen peroxide can be generated in situ to be integrated into advanced oxidative processes when there is a demand for H₂O₂ as a reagent in concentrations of up to 350 mg/L and under the conditions used in this work.

References

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between the values, despite the considerable increase in current.

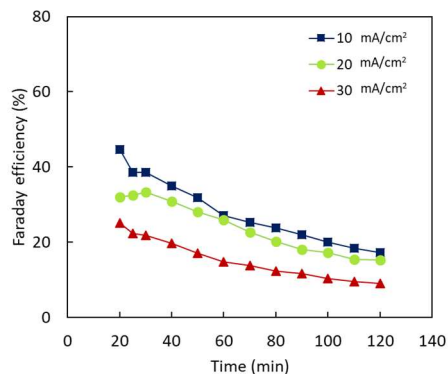


Figure 2. Faraday efficiency at different current densities as a function of operating time.

Figure 3 shows a comparison of the energy consumption obtained for each current density. It is clear that, invariably, an increase in energy consumption was observed with an increase in current density.

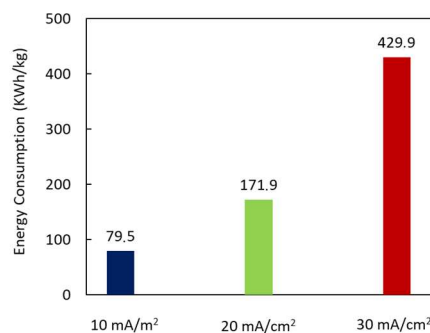


Figure 3. Energy consumption at different current densities.

Therefore, the best current densities evaluated in this study would be 10 and 20 mA/cm², since the final concentrations obtained in 120 minutes of electrolysis were 196.7 and 350.0 mg/L, current efficiency of 17 and 15%, as well as energy consumption of 79.5 and 171.9 kWh/kg, respectively.